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Investigation of the Kinetics of
Crystallization of Molten Binary
and Ternary Oxide Systems

Summary and Quarterly Status Report No. 7

Contract NASW-1301

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Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems

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Contract No. NASW-1301

SUMMARY

Contract NASW-1301 was signed for a period of one year initially. The first extension of this contract lengthened the research program to 21 months so that the research effort has covered the period from September 1, 1965 through May 31, 1967. This report both summarizes all of the research carried out in the nine-month contractural extension, September 1, 1966 through May 31, 1967 and serves as a detailed quarterly report for the seventh quarter of the program, March 1, 1967 through May 31, 1967. Similar summary reports will be prepared in the tenth and thirteenth quarters while details of the first year's work on the contract are contained in UARL Report F910373-4.

Sixty-six additional new glass compositions were devised, successfully melted, and characterized at least in part since September 1, 1966. These glasses are grouped in five series, the National Bureau of Standards calcium-aluminate glasses formed the basis for calcium-yttria formulations, Stevels "invert" glasses were extended to include "invert" glasses based on silica-alumina and silica-yttria, the UARL "cordierite-sapphirine" composition field was extended to include equal or greater amounts of rare-earth oxides, this same series of UARL compositions were further modified by substituting calcia for magnesia, and finally the UARL series was modified by replacing the alumina as a constituent by calcia, adding several additional glass-making oxides to lower the liquidus, to lower the density, to increase the working range, and to increase the viscosity, and increasing the rare-earth concentrations to the single largest constituent category.

These glasses together with those prepared in the first year's program give a total of 150 new experimental compositions requiring characterization when promising. Of this number, viscosity-temperature data has been obtained for twenty-nine varieties, **Young's** modulus measured for thirty-eight species in the bulk, and twenty-seven compositions have successfully been drawn into fibers by mechanical methods and their Young's moduli measured by sonic methods.

A micro-furnace has been designed to permit microscopic observations of crystals growing in molten oxides and used to establish growth curves for cordierite and sapphirine crystals in several molten oxide systems. An enlarged platform furnace usable in air at temperatures to 1800°C was built which, when used in conjunction with a 20 cm3 platinum crucible with properly shaped nozzle, makes possible the production of mechanically drawn glass fibers without the necessity of using the massive very expensive one-hole platinum bushing customarily employed in this type of research. Equipment for continuously monitoring the electrical conductivity of molten oxide systems was devised and used to study crystallization kinetics **of** molten oxide systems. Young's modulus by mechanical methods has also been measured **for** one glass fiber species.

The work to date has resulted in several glass compositions with values for Young's modulus to density completely comparable to any glass now available commercially and which do not require the addition of any toxic materials.

Glass	Density gms/cm^3	Modulus $psix10^6$	Modulus/Density $psix10^6/gms/cm^3$
Owens-Corning Commercial E	2.55	10.5	4.12
Owens-Corning Commercial X-994	2.485	12.6	5.07
Owens-Corning Pilot Plant Y(BeO)	2.38	14 to 15	5.88 to 6.29
*Owens-Corning U.S. 3,122,277 (BeO)	2.8376	17.18	6.07
*Houze Glass - U.S. 3,044,888	2.5875	15.47	5.98
*UARL 68-2	2.6295	16.35	6.22
*UARL 67-3	2.6535	16.33	6.17
*UARL 70	2.73	16.77	6.14
*UARL 62-3	2.7036	16.25	6.02

*All of these glasses were prepared, melted, fiberized, and tested in identical procedures at UARL for direct comparative evaluation. The data for the first three glasses is published data.

Other glasses have **also** been prepared at UARL with a higher elastic modulus but these have a higher density so that modulus to density ratio is inferior to those tabulated above at this time. Research on lowering the density without decreasing the modulus is in progress.

INTRODUCTION

This is the seventh quarterly status report as well as the second summary report for Contract NASW-1301 entitled, "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems". This seventh quarter of the contract started March 1, 1967 and ended May 31, 1967, while the period summarized started September 1, 1966 and ended May 31, 1967 and represents the first extension to the contract. The primary objective of this program is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the effect of anti-nucleating agents on the observed crystallization rate for systems which tend to form complex three dimensional structures. Determination of the crystallization rate is carried out by continuously measuring the viscosity and electrical conductivity of the molten system as a function of time and temperature with checks of surface tension at selected temperatures. In this nine-month period an important supplementary method for determining the crystallization rate, namely direct microscopic examination of samples in a microfurnace has been introduced and has proven to be very helpful, Glass formation is greatly increased by employing cooling rates high enough to defeat the formation of the complex many-atom three-dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis.

SELECTION AND PREPARATION OF GLASS SYSTEMS FOR PRELIMINARY EVALUATION

Sixty-six new glass batches were formulated, mixed and melted in the nine-month period summarized together with new preparations of sixty-five older glass formulations to provide additional material for property evaluation. These sixty-six compositions are listed in Table I. Thirteen of the new glasses were based on calcia-alumina or alternately calcia-yttria as the glass formers and are like those prepared by the National Bureau of Standards (Ref. 1) although with extensive modifications and additions. Thirteen more of the new glasses were silica-alumina "invert" glasses and silica-yttria "invert" glasses with extensive variations. As will be recalled from several of the earlier quarterly reports on this contract, these "invert" glasses were developed by Stevels (Ref. 2) and may contain as little as 34 mol % silica. The composition of such glasses is indicated by a parameter Y designating the average number of bridging ions per SiO_4 tetrahedron and calculated from the expression

$$Y = 6 - \frac{200}{P} \text{ where } P = \text{mol \% } SiO_2$$

so that when P = 33-1/3, Y = 0 and the SiO_4 groups are isolated; when P = 40%, Y = 1 and on the average SiO_4 groups appear in pairs. Properties of these glasses such as viscosity at a given temperature, the viscosity activation energy, thermal expansivity, electrical deformation loss go through extreme values when the parameter Y passes through the value of 2.0. There is every reason, therefore, to believe that mechanical properties such as Young's modulus will show a similar parabolic relationship when plotted against the parameter Y, climbing steeply as Y decreases from 2 to 1 and then falling off again.

The third group of glasses belongs to the original oxide system selected for investigation, cordierite or $Mg_2Al_4Si_5O_{18}$ - a three-dimensional ring former but with additions of rare-earth oxides so large that the total weight contribution of the cordierite components is nearly the same as that of the selected rare-earth oxide. It should be mentioned that in this preliminary exploration only pure rare-earth compounds were used so that the data could unequivocally be interpreted but in actual glass making operations a much less costly and impure mixed rare-earth formulation could be readily substituted. The fourth group of glasses prepared likewise belongs to the cordierite field but with the same massive proportions of rare-earth oxides and with the replacement of magnesia by calcia. The fifth group of glasses again is of the generic cordierite variety but with alumina replaced by calcia, with massive rare-earth proportions, and with the addition of materials such as ceria to lower the liquidus, with lithia to aid as a flux, with zirconia to improve the modulus and viscosity-temperature relationships and with titania to lower the surface tension.

Typically, these glasses are prepared in 500 gram batches in high purity (99.9%) alumina crucibles in air in the Super-Kanthal hairpin kiln shown in Fig. 1. Starting materials used are 5 micron particle size high purity silica, high purity alumina of 325 mesh, high purity precipitated magnesia, 99% purity grade rare-earth oxalates and similar laboratory materials. These ingredients are completely mixed dry by tumbling and briquetted so as to be easily handled (Fig. 1 shows the addition of pellets to already molten glass). The materials yield in general a water-white optical grade glass free of seed and bubbles due to the fining action of the oxalates when held at a temperature of 1540 C or higher for two hours. Alumina crucibles of even slightly lower purity (99.3 to 99.7%) cannot be used, nor can the temperature of 1540 to 1560 C be exceeded in general, even with the highest purity alumina crucible. More refractory glasses are melted, therefore, either in platinum alloy crucibles in the platform kiln described later or in an atmosphere of argon in a tungsten crucible in the tungsten furnace described in last year's summary report.

KINETICS OF CRYSTALLIZATION RESEARCH

The kinetics of crystallization of the glass systems investigated under this contract are determined from continuous measurement of the electrical resistivity and viscosity of the system and by direct microscopic observation of the behavior of the glass batch at various temperatures using a recently constructed microfurnace. These measurements together with property measurements such as density, Young's modulus, and fiberizability serve to characterize the glass system studied.

Electrical Conductivity Measurements

To study the electrical conductivity of the molten oxides as a function of time and temperature, the glasses were melted as described above and broken up and packed into the tungsten crucible. This crucible is made to serve as a conductivity cell by introducing a tungsten ball, one-quarter inch in diameter, on the end of a tungsten rod into the exact center of the crucible and by tying a tungsten rod to the outside of the crucible with 25 mil tantalum wire. The whole assembly is then placed in the tungsten resistance furnace and heated until the glass is completely remelted. Power to the furnace is then turned off and the electrical conductivity of the molten oxide system is measured continuously through the solidification process as the furnace cools. The temperature of the crucible is measured at thirty-second intervals to obtain the required data connecting electrical conductivity with crystallization or lack of crystallization rates.

The actual measurement of the electrical conductivity is carried out by connecting externally the UARL "log ohmmeter" to the two leads from the tungsten crucible conductivity cell. These leads are brought out of the furnace using vacuum-type electrical lead-ins. The log ohmmeter is designed to measure resistance from 10^{-1} ohms to 10^{+6} ohms and generates a d-c signal voltage proportional to the logarithm of the resistance. The scale for this instrument is divided into six ranges: 10^{+6} ohms to 10^{+5} ohms, 10^{+5} to 10^{+3} ohms, 10^{+3} to 10^{+2} ohms, 10^{+2} ohms to 10 ohms, 10 ohms to 1 ohm, and 1 ohm to 10^{-1} ohm. Over each range, the amplitude of the signal applied to the unknown resistor and the sampling resistor are adjusted so that the power dissipated in the sample is less than 500 microwatts, and the sample resistor is less than 6.5 percent of the resistance being measured.

In each range position, a constant amplitude, 1000 cycle/sec, sinusoidal voltage is applied to the unknown and the current through it measured by a sampling resistor. This signal is passed through a series of filters consisting of a band-pass filter from 800 to 2000 cycles/sec, a twin-tee notch

filter at 60 cycles/sec and a twin-tee notch filter at 180 cycles/sec in cascade. These filters effectively remove the large amount of noise generated in the sample by the massive (1000's of amperes) 60 cycle heater current present in the tungsten furnace. The signal is then linearly amplified by a guarded amplifier to a level of 0.5 volts p-p to 50 volts p-p and used to drive a power amplifier. The power amplifier isolates the guarded amplifier from the detector. The d-c voltage from the detector is then applied to the logarithmic converter which puts out a d-c voltage proportional to the logarithm of the input voltage. A unity gain operational amplifier following the logarithmic converter provides the low output impedance necessary to drive the strip chart recorder.

The electrical conductivity device has been used successfully for several of the molten oxide systems. However, the measurements did not seem as useful in selecting those molten oxide systems for further study as did direct measurements of viscosity, elastic moduli, and fiberizability. Attention has been concentrated on these latter measurements, therefore, it is planned to resume electrical conductivity studies early this Fall at a time when they can be supplemented by direct optical microscopic observations.

Viscosity Measurements

The device initially used to measure the viscosity of the molten oxide systems at high temperature is the Brookfield Synchro-Electric Viscometer.* The principle of operation of the device is simple. A cylinder or disc or spindle is rotated in the fluid under test through a beryllium-copper spring. The deflection of the spring is read on a dial. The dial reading with the usual disc is multiplied by a simple constant to obtain the resulting viscosity at the particular rotational speed or when special design spindles are used, the device is calibrated through the use of oils of known viscosity. Measurements made at different speeds are used to describe the complete flow properties of the material at hand.

The Brookfield viscometer had never been used before at temperatures as high as those likely to occur in this contract. However, this merely meant that the device must be equipped with a long shaft entering the furnace and with a spindle of suitable high temperature material. Tungsten was selected as the material for both the spindle and shaft because of its known compatibility with all the molten oxide systems investigated to date, and Brookfield Engineering Laboratories then designed a suitable tungsten spindle. This tungsten spindle and the Brookfield viscometer were calibrated using the

*Trade-mark, Brookfield Engineering Laboratories, Inc., Stoughton, Mass.

National Bureau of Standards standard viscosity oil "P" by placing an exact silica replica of the tungsten crucible normally used in the constant temperature bath, filling the silica crucible with oil "P" and running the tungsten spindle in the crucible in such a way as to exactly simulate high temperature operations. With this constant temperature bath, oil temperatures could be held constant to within ± 0.005 C in the range from -5° to + 107 C. With this bath, the necessary calibration data was obtained for the tungsten spindle.

The Brookfield viscometer and tungsten spindle with its elongated shaft were installed on the tungsten resistance furnace as shown in Fig. 2. The spindle is brought out of the tungsten furnace through a high vacuum fitting. Originally the spindle is at rest, the ground glass previously melted in other furnaces is placed in the crucible, the whole system is evacuated, flushed with purified argon by loosening the vacuum fitting and allowing the argon (at a positive pressure of 5 in. of water) to stream out, re-evacuated, and refilled with purified argon. The system is heated until the glass is molten as judged by visual examination and the tungsten spindle inserted into the melt and positioned at the proper depth. The temperature of the furnace is adjusted to the desired values and the viscosity of the selected experimental glass is measured at the various temperatures.

Viscosity-temperature curves were measured for a number of experimental glass compositions with the results shown in Figs. 3, 4, 5, and 6 and as tabulated in Table II and summarized in Table 111. It is immediately apparent that many of these experimental glasses have much steeper-temperature viscosity curves than a typical "hard" glass. Successful formation of fibers from such glasses demands accurate temperature control, care in sizing the orifice through which the glass is drawn, and variable speed drawing equipment. However, with considerable attention to such details it has proven possible to successfully fiberize all of these glasses in our laboratory using the equipment described in a later section. In Table III where all of the viscosity data obtained to date is summarized by listing those temperatures at which a given glass batch has a viscosity of approximately 300 poises, it will be noted that the glasses melted to date have a wide range of refractoriness. In general, as will be shown later, only the more refractory of these glasses have proven interesting in the search for glasses that can be fiberized and which have an unusually high modulus.

Use of the Microfurnace for Direct Optical Observation of the Kinetics of Crystallization

The direct microscopic observation of the kinetics of crystallization of two crystal species, cordierite and sapphirine originating in molten MgO-Al_2O_3-SiO_2 systems was made possible by the construction of a microfurnace.

This UARL microfurnace design owes much to the earlier furnace constructed by Morley (Ref. 3) for exactly the same type research, namely, the study of crystallization kinetics in molten glass. The microfurnace consists essentially of a platinum-10% rhodium tube, 0.250 in. O.D. and with a wall thickness of 3 mils, which is damped between the two copper bars (0.125 in. x 0.500 in.). A circular shelf of platinum is welded to the inside of the tube, and the crucible is placed in a 0.128 in. hole in this shelf. Crucibles are fabricated by cutting platinum tubing (0.125 in. dia with 5 mil wall thickness) into pieces 0.065 in. long and then pressing them in a die so that they form a 40 degree included angle.

Figure 7 shows the microfurnace without radiation shielding. Subsequently radiation shielding was found necessary and was added by welding two rings of 0.057 in. Kanthal wire to the nichrome plates at the two ends of the heater tube. An inner shield of 4 mil platinum-rhodium sheet and an outer shield of 5 mil nichrome sheet were welded to the inner nichrome wire ring that is on the lower nichrome plate. Two 5 mil nichrome shields were welded to the outer nichrome wire ring on the upper circular nichrome plate.

Figure 7 also shows the 1/8 in. dia copper tubing which is used to supply water-cooling to the copper electrical connectors. The power supplied the furnace comes from a filament transformer of 0.975 KVA capacity and a 20 ampere Variac. To attain a temperature of 1400 C a current of 140 amperes at 1.1 volts (60 cycle a-c) has proven adequate.

The entire experimental arrangement with the exception of the power supply is shown in Fig. 8. It comprises the microfurnace, microscope and camera, micromanipulator used to weld and position the thermocouple, the x-y recorder used for plotting time-temperature response of the furnace, and the 3 mil platinum-platinum 10% rhodium thermocouple carefully positioned in the center of the furnace. Experience has shown that the furnace temperature can be maintained to within ± 4 C at 1250 C.

In actual use, the crucible is inserted into the furnace, a large fragment of glass is placed in the crucible and the crucible then heated. Smaller glass fragments are later added to completely fill the crucible. The glass is then heated until all of the bubbles disappear and then cooled to the temperature selected for crystal growth observation. The thermocouple is then lowered into the melt and photographs are taken of the crystals growing on the thermocouple at selected time intervals. Seed crystals can be grown on the thermocouple by placing it in the melt and then withdrawing it to a cooler part of the furnace, a step that may or may not be necessary depending on the composition of the glass under investigation. High-speed film is used (Polaroid-ASA 3000) and good quality pictures are readily obtainable. The actual sizes of the crystals in the photographs can readily be obtained by calibrating the optical system employed.

With this equipment measurements of the rate of growth of cordierite in Batch 1 were made and sufficient data (Table IV) were taken to partially delineate a plot of the rate of growth versus temperature (Fig. 9). The features of this curve which are similar to the curve expressing the rate of growth of cordierite in Batch 1-B (Fig. 9) are: measurable growth rates begin at about 950°, the maximum occurs at 1200°-1250°, very low growth rates at 1375° to 1410°, periods of no measurable growth for periods of 5 and 9 min, and at higher temperatures there are rates of solution of 20 μ/min. The main difference from the growth-rate curve for Batch 1-B is that the growth rate is much higher, approximately 500 μ/min as compared to about 300 μ/min for Batch 1-B. The composition of Batch 1 is 50.3 wt % SiO_2, 30.5 wt % Al_2O_3, 19.45 wt % MgO, and the composition of Batch 1-B is 55 wt % SiO_2, 30 wt % Al_2O_3, and 15 wt % MgO. The difference in these compositions is that Batch 1 has about 5 wt % less silica and 5 wt % more magnesia, and might be expected to have a lower viscosity than would Batch 1-B at the same temperature.

Figure 9 also shows that the rate of growth at the high temperature end of the curve approaches the liquidus temperature tangentially and that the curve is not symmetrical as the liquidus temperature is exceeded, that is, as the rate of growth changes to the rate of solution. The growth curve for Batch 1-B has this same feature. Further conclusions will be possible as soon as more data are taken with Batch 1. Our few data concerning the asymmetry in these curves are supported by a paper presented at the annual meeting of the American Ceramic Society, by Drs. G. S. Meiling and D. R. Uhlmann (Ref. 4). These authors, in a paper entitled, "Crystallization and Melting Kinetics of Sodium Disilicate", describe a pronounced asymmetry in the growth-rate and melting rate curves in the vicinity of the melting point.

Several interesting crystal habits have been observed during the devitrification studies. The first of these is the habit that has been observed for sapphirine in Batch 1-B. Figure 12 shows sapphirine photographed at a temperature of 1222 C with a magnification of 40 times, while Fig. 13 shows sapphirine crystals which were photographed at room temperature at a magnification of 200 times. This unusual crystal habit appears to consist of two or three crystals joined at their mid sections. The work of Keith and Schairer (Ref. 5) describes sapphirine as occurring as elongated and usually faceted monoclinic crystals and reports one twinned crystal but made no observation of the twinning. Our work has revealed many dendritic habits of sapphirine which are dependent upon the growth rate, but our observations are made at temperatures considerably below the liquidus. Long hollow prisms of cordierite have also been observed, similar to those reported by Schreyer and Schairer (Ref. 6). These are shown in Figs. 10 and 11. These photographs were made at room temperature of cordierite which was grown in Batch 1. The crystals in Fig. 11 were originally completely solid, and became hollow on the ends when the growth rate was increased. It has also been possible to start with hollow crystals, and grow them at a slower growth rate until they become solid.

CHARACTERIZATION OF EXPERIMENTAL GLASSES IN THE BULK

The experimental glasses melted were characterized by measuring Young's modulus on the bulk specimens and an evaluation of their glass making and fiberizability ratings.

The equipment used for the measurement of Young's modulus originally was satisfactory if glass specimens two inches **or** greater in length were available. But for many glasses without allowing undue lengths of time working out the proper annealing cycle, the longest lengths available are only approximately one inch. To carry out significant measurements on such short samples it was necessary to put together equipment capable of operating at much higher frequencies. This in turn meant purchasing much higher fidelity components.

Equipment selected for improved measurements are shown in Fig. 14. This system shown as a block diagram measures the resonant frequency of glass rods in the region between 1000 and 40,000 Hz. The sample is supported at the nodal points for the fundamental resonance by thin flexible supports that have a resonant frequency below 1000 Hz. A 30 watt driver unit below the center of the sample drives a column of air which in turn excites the sample. The vertical displacement of the end of the bar is detected by the transducer, a high quality semiconductor phonograph cartridge and tone arm adjusted for a tracking force of approximately 0.1 gram. The differential output from the transducer is amplified by a preamplifier which also supplies excitation to the transducer. The output of the preamplifier is passed through a high pass R-C filter to remove low frequency noise due to building and support vibrations and is amplified in a guarded differential amplifier. This amplified signal is displayed on a CRO and peak detected to drive the vertical axis of an x-y recorder.

Primary excitation is supplied to the driver unit by a variable frequency audio oscillator through an audio amplifier. A potentiometer mechanically coupled to the frequency control on the oscillator supplies a d-c voltage to the horizontal axis of the x-y recorder proportional to the logarithm of the driving frequency.

With the above system, any spurious resonances due ***to*** the driver unit, transducer or supporting structures will appear the same for different samples and can thus be eliminated from the data by the operator. Resonances with amplitudes smaller than those from extraneous sources can be easily resolved by comparative recordings for different sample lengths.

The over-all system has a frequency response from 3000 to 40,000 Hz with an amplitude variation of 3db.

The improved equipment proved much simpler to operate than its immediate predecessor. Almost all of the results tabulated in Table V, Young's Modulus for Bulk Samples of Experimental Glasses, were obtained with this equipment. The degree of consistency obtainable with this equipment has proven to be entirely dependent on sample preparation and not on the test itself since all of the variation can be traced to variances in the machined dimensions of the small samples which are typically 1.800 in. long, 0.1240 in. wide, and 0.1240 in. high. These samples are prepared by grinding by a local lens maker and tolerances on these dimensions of ± 0.003 in. are the best he is able to achieve especially since these glasses are harder than the usual optical glasses. Several of the glasses prepared late in this period show an improvement of greater than 10% compared to the best glasses prepared during the first year of the contract.

Evaluation of Glass Forming Characteristics and Fiberizability

Oxide materials previously melted in the standard kilns using the procedures described earlier in this report furnish the starting materials used in this phase of our research. From the previous firing in the kiln they have emerged either as fully melted glasses, glass and crystalline masses, or materials that appear similar to clinkers or cinders. One chooses a sufficient amount of this material to fill a 15 milliliter platinum crucible. The material is then crushed or ground to approximately 10 mesh size and placed in the platinum crucible. The platinum crucible then is placed on the motor-driven platform of the Super-Kanthal hairpin furnace. The furnace platform is raised rapidly until the crucible is in the center of the furnace, which has previously been heated to the desired temperature. The crucible is then kept at the desired temperature for a time varying from one-half hour to two hours dependent of the particular glass under investigation and is then lowered as rapidly as possible. As soon as the crucible becomes accessible, one man picks it up in tongs and a second man dips a twenty mil platinum wire into the molten glass and runs away from the crucible as rapidly as possible. Usually in this manner, it is possible to hand draw a glass fiber 2 to 5 mils in diameter and thirty to forty feet long. The platinum wire is, of course, mounted in a glass tubing handle. In this simple fashion, it is readily possible to obtain crude ideas of the glass forming characteristics and fiberizability of the various glass batches at a variety of temperatures. The Super-Kanthal kiln using experimental types Super-Kanthal hairpin elements readily obtains a temperature of 1800 C in air. Glasses, which yield easily long hand-drawn fibers in this test or alternately which form vitreous buttons when the contents of the platinum crucible are poured on a graphite slab, are selected for further evaluation.

CHARACTERIZATION OF GLASS FIBERS PRODUCED FROM EXPERIMENTAL GLASS COMPOSITIONS

Property Measurement on Hand-Drawn Fibers

Originally, it was felt that the hand-drawn fibers produced in the fiberizability test of bulk glasses could be used for the evaluation of the properties of glass fibers. It quickly became evident, however, that no matter how carefully hand-drawn fibers were prepared, they tended to show a distorted elliptical cross-section. In Fig. 15 the least distorted hand-drawn fibers obtained are shown in cross-section in contrast with a 3 mil platinum wire (white) and in Fig. 16 the most distorted hand-drawn fiber specimens encountered are shown. The distortion is so great as to make it impossible to obtain a meaningful value for the average cross-section of such fibers and this fact made the values of Young's modulus deduced by dead-weight mechanical testing procedures extremely untrustworthy. Despite this fact, many of the previous investigators have published such data leaving the available literature with a very confusing collection of data. UARL published similar data in the fifth quarterly report on this contract and we are now convinced that these values are largely meaningless.

Mechanical Drawing of Glass Fibers from an Orifice

The above problems encountered in attempting to obtain a reliable value for Young's modulus on hand-drawn fibers made it quickly obvious that it was time to switch to mechanical drawing of the experimental glass fibers. Normally this is done by purchasing massive platinum-rhodium bushings of proven design, But in our case several bushings would be necessary since the experimental glass compositions vary so widely that the life-time of such a bushing might be very limited. Several such bushings would represent an expenditure for materials three to four times as great as the program material cost to date. Fortunately, it has proven possible using the platform furnace pictured in Fig. 17 to substitute a relatively inexpensive 20 cc platinum crucible for the platinum bushings customarily employed. To make this substitution it was necessary to reinforce the bottom of the platinum crucible in a small central area by welding foil to the crucible until a thickness of 3/16 in. was obtained. This central area was then tapered reamed to form an orifice 0.088 in. at top, 0.063 in. at bottom and 3/16 in. long. In addition, water cooling almost directly beneath the crucible had to be introduced into the furnace as well as a ring orifice arrangement for cooling the fiber as it forms with helium jets. This equipment has now been extensively tested and proven to yield glass fiber that is very close to circular, approximately one mil in diameter when pulling speeds of 4000 ft/min are employed, and suitable for improved modulus determinations. The equipment arranged for mechanical drawing of fibers is shown in Fig. 18.

The improvement in the roundness of the glass fibers which resulted by mechanical drawing is shown in Figs. 19 and 20 where again the white specimen is a 3 mil platinum wire in cross-section. It is further obvious that much finer fibers can be drawn mechanically than were achieved by hand-drawing. The degree of circularity achieved in the mechanical drawing process is best realized by examining Table VI where typical microscopic measurements of the diameter of given samples are listed for each 45° rotation of the sample. This degree of roundness achieved is sufficient to eliminate departure from circularity as a source of error in modulus evaluation.

Table VII lists the twenty-six experimental glasses which have been successfully used in the mechanical drawing of glass fibers to date. These twenty-six glass compositions are approximately half the experimental glass compositions studied to date so that our experience indicates about one out of every two experimental glasses can be used successfully for the production of mechanically drawn fibers. The remaining UARL glass compositions will be tested in the next quarter.

Young's Modulus of Glass Fibers as Measured with Sonic Equipment

Table VII lists the values found for Young's modulus for those glasses which could successfully be drawn by mechanical means. Glass melt 82-2 was made from the teachings found in U.S. 3,044,888 and melt 83-1 from the doctrine of example 4 of U.S. 3,127,277 in order to provide samples of the most outstanding glasses found in the literature. Glass 83-1 contains 11.0% beryllia by weight. All other glasses in the table are original with UARL. All glasses were prepared, drawn into fibers, and tested in identical fashion so that the comparative data of the table should be highly reliable even though the absolute numbers assigned to the values of Young's modulus may be in error by a constant multiple. Tests marked FAB were carried out at Fabric Research Laboratories by their personnel and those marked UARL were carried out here by our personnel on two different pieces of the same model Dynamic Modulus Tester PPM-5R manufactured by H. M. Morgan Co., Inc., Cambridge, Massachusetts. This equipment is pictured in Fig. 21. It functions by measuring the velocity of a longitudinal sound wave in lightly loaded fiber sample. It has been widely sold and distributed and used to measure the elastic modulus of synthetic fibers and yarns, inorganic and refractory fibers and yarns, wires, polymeric fibers, hair, felts, and other extensively varied types of fibers.

This method of testing is independent of the measurement of the diameter of the fiber and depends instead only on the longitudinal sound velocity and the density. The densities of the samples in the table were largely measured by flotation techniques by A. W. LaDue of the Hartford Division of The Emhart Corporation. Thus, the data in the table should be largely independent of any bias by UARL personnel.

Table VII shows that several of the UARL experimental glasses have better elastic modulus to density ratios than the best of the glass compositions given in the literature. Yet, these UARL glasses contain no toxic ingredients. Further research, of course, is necessary before any of these glasses can be considered a developed product but the indications are that such research is justified.

Young's Modulus of Glass Fibers Measured by Mechanical Testing

An alternative method for determining Young's modulus of glass fibers is to use a dead-load stress-strain procedure in which the displacements of two points of the test fiber is obtained by using linear variable differential transformers (LVDT). It will be noted from Table VIII that the result for UARL experimental glass No. 114 by this method is in good agreement with that obtained by sonic methods and shown in Table VII. However, this method requires tedious, repetitive, and meticulous microscopic measurements of the diameters of the glass fibers to avoid large error since the fourth power of' the diameter enters the calculation. Additional UARL glass fibers will be evaluated by this procedure again using external facilities and personnel at Lowell Technological Institute so as to avoid experimenter bias. Many of these results should be available early in the next quarter.

Supplemental Capital Equipment Available for the UARL Program

Capital equipment available for this program has recently been supplemented by UARL funds to include the vacuum and inert gas melting and casting furnace shown in Fig. 22. The use of this equipment should enable us to cast and anneal a variety of forms of the experimental glasses in bulk form, thus both expediting and making more meaningful property measurements on such materials.

CONCLUSIONS

1. The direction of approach used in the UARL program of studying the kinetics of crystallization of molten oxide systems likely to form complex three-dimensional molecules continues to yield glass fibers with superior values of elastic modulus and should, therefore, be continued.

2. This research should now both concentrate on the search for optimum glass compositions in the fields studied to date and should continue to explore wholly new combinations of unusual glass making oxides.

3. Part of the research effort should be devoted to changing the compositions of the higher modulus glasses already found by progressive substitution to lower density without any corresponding decrease in modulus, to substituting inexpensive mixtures of rare-earth oxides for the costly materials currently being used, and to adding any necessary ingredients to avoid devitrification and lengthen the working range.

4. Fibers from the more promising experimental glass compositions should be freshly prepared for strength tests.

PERSONNEL ACTIVE ON PROGRAM

Personnel active on the program throughout the nine month contractural extension have been J. F. Bacon, principal investigator, and Norman J. Chamberlain, senior experimental technician. They were aided on numerous occasions by Louis J. Tempel, Jr. of the UARL Instrumentation Section. Robert B. Graf constructed the microfurnace and used it to carry out the optical studies of crystallization kinetics. Charles E. Shulze of the Materials Sciences Section constructed the dead-weight stress-strain equipment and used it to obtain the data for Young's modulus shown in Table VIII. Liaison throughout the program has been carried out by Peter A. Stranges of the UARL Washington Office.

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TABLE I

Composition of Experimental Glasses

1. A Series of Glasses Based on Calcium Alumina and Calcium Yttria

Ingredient	Batch No. (amounts of ingredients in grams) 84	85	86	87	88	89	90
Calcium Carbonate	349	384	384	349	384	384	250
Alumina	210	235	235	---	---	---	---
Barium Carbonate	65	---	---	65	---	---	---
Magnesium Oxide	25	25	25	25	25	25	100
Zirconium Carbonate	28	---	28	28	---	28	28
Tantalum Oxide	---	25	---	---	25	---	---
Yttrium Oxalate	---	---	---	562	625	625	625
Silica	---	---	---	---	---	---	---

	91	92	93	94	95	96
Calcium Carbonate	178	89.5	250	268	295	295
Alumina	---	---	210	---	---	185
Barium Carbonate	---	---	65	65	---	---
Magnesium Oxide	140	190	25	25	25	25
Zirconium Carbonate	28	28	28	28	28	28
Tantalum Oxide	---	---	---	---	---	---
Yttrium Oxalate	625	625	---	562	562	---
Silica	---	----	50	40	50	50

2. A New Series of "Invert" Glasses Based on Alumina and Yttria

	Batch No. (amounts of ingredients in grams) 97	98	99	100	101	102	103
Silica(SiO_2)	261.5	209.5	158.8	120.5	120.5	221.0	213.5
Alumina(Al_2O_3)	47.80	58.1	67.4	76.0	122.7	92.0	88.0
Yttrium Oxalate	---	---	---	---	---	---	---
Potassium Carbonate	75.5	92.4	107.5	120.7	102.5	---	---
Lithium Carbonate	---	---	---	---	---	66.7	64.3
Calcium Carbonate	47.1	57.1	66.3	74.5	63.0	90.3	86.7
Strontium Carbonate	69.2	77.1	97.6	110.0	93.0	---	127.5
Zinc Carbonate	---	---	---	---	---	113.6	---
Barium Carbonate	93.7	113.7	134.3	148.7	125.5	---	---
Magnesia (MgO)	---	---	---	---	---	36.25	34.85

TABLE I (Cont'd)

	104	105	106	107	108	109
Silica(SiO_2)	191.5	181.0	136.0	229.5	281.5	116.5
Alumina(Al_2O_3)	79.5	---	---	---	---	---
Yttrium Oxalate	---	442.0	509.0	378.0	305.0	703.0
Potassium Carbonate	126.0	---	---	---	---	---
Lithium Carbonate	---	54.4	62.0	46.1	37.1	43.5
Calcium Carbonate	77.7	73.7	84.5	62.5	50.4	60.9
Strontium Carbonate	115.5	---	---	---	---	---
Zinc Carbonate	---	92.1	105.4	78.4	63.1	76.4
Barium Carbonate	---	---	---	---	---	---
Magnesia(MgO)	31.35	29.6	33.9	25.15	20.3	24.55

3. Additional Glasses Based on Cordierite

	Batch No. (amounts of ingredients in grams) 110	111	112	113	114	115
Silica(SiO_2)	256	224	224	167.75	187.0	138.0
Alumina(Al_2O_3)	175	221.2	221.2	123.0	138.0	140
Basic Magnesia Carbonate	137.2	130.3	---	---	---	---
Magnesia(MgO)	---	---	53.40	34.25	38.4	40.75
Cerium Oxalate	---	---	---	379	---	389.5
Yttrium Oxalate	---	---	---	---	360.5	---
Samarium Oxalate	---	---	---	---	---	---
Zirconium Carbonate	---	---	---	---	---	---
Lanthanum Oxalate	---	---	---	---	---	---

	116	117	118	119	120	121
Silica(SiO_2)	136.5	149.0	113.5	165.5	146.5	104.1
Alumina(Al_2O_3)	138.5	48.75	---	54.25	---	96.0
Basic Magnesia Carbonate	---	---	---	---	---	---
Magnesia(MgO)	40.35	35.45	27	39.40	34.85	26.6
Cerium Oxalate	---	677	773	---	---	588
Yttrium Oxalate	492	---	---	644	853	---
Samarium Oxalate	---	---	---	---	---	---
Zirconium Carbonate	---	---	---	---	---	---
Lanthanum Oxalate	---	---	---	---	---	---

TABLE I (Cont'd)

	122	123	124	125	126
Silica(SiO_2)	69.8	101.0	104.5	178.5	165.5
Alumina(Al_2O_3)	83.75	92.5	95.75	181.5	127.5
Basic Magnesia Carbonate	---	---	---	---	---
Magnesia(MgO)	23.0	25.75	26.70	52.75	30.95
Cerium Oxalate	774	---	---	---	---
Yttrium Oxalate	---	---	---	---	460
Samarium Oxalate	---	602	---	---	---
Zirconium Carbonate	---	---	---	98.1	---
Lanthanum Oxalate	---	---	592	---	---

4. Cordierite Glasses with Calcia Substituted for Alumina

	Batch No. (amounts of ingredients in grams)					
	127	128	129	130	131	132
Silica	230	275	193	225	270.5	185.0
Alumina	64.5	44.5	87.8	63.1	43.6	83.6
Magnesia(MgO)	51.0	35.0	74.1	---	---	---
Calcium Carbonate	---	---	---	128.3	74.1	164.0
Yttrium Oxalate	384.0	393.0	382	375	388	372.0
Beryllium Carbonate	---	---	---	---	---	---
Lanthanum Oxalate	---	---	---	---	---	---
Cerium Oxalate	---	---	---	---	---	---

	133	134	135	136	137	138
Silica	229.5	244.5	258.0	242.5	223.0	173.15
Alumina	64.8	69.0	125.5	119.75	108.35	96.75
Magnesia(MgO)	25.65	---	92.0	88.1	79.85	71.15
Calcium Carbonate	62.8	---	---	---	---	---
Yttrium Oxalate	384	409.0	---	---	---	---
Beryllium Carbonate	---	74.5	---	---	---	---
Lanthanum Oxalate	---	---	55.7	106.9	192.3	346.0
Cerium Oxalate	---	---	---	---	---	---

TABLE I (Cont'd)

	139	140	141	142	143	144
Silica	114.15	167.25	107.75	153.5	111.5	33.6
Alumina	76.75	83.6	72.25	87.35	109.5	165.0
Magnesia(MgO)	56.55	66.35	49.25	18.25	24.1	---
Calcium Carbonate	---	---	---	144.5	179.5	279
Yttrium Oxalate	---	---	---	361	360	337
Beryllium Carbonate	---	---	---	---	---	---
Lanthanum Oxalate	547	332	514	---	---	---
Cerium Oxalate	---	41.6	64.3	42.1	42.2	39.4

5. A New Glass Series

	Batch No. (amounts of ingredients in grams)					
	145	146	147	148	149	150
Yttrium Oxalate	404	390	---	---	---	---
Lanthanum Oxalate	---	---	417	402	---	---
Cerium Oxalate	47.8	45.6	41.7	40.2	40.7	39.5
Samarium Oxalate	---	---	---	---	431.0	418
Silica	160.5	155	142.0	130.3	139.0	134.5
Calcium Carbonate	71.2	106.7	112.5	94.2	115.3	98.0
Magnesia(MgO)	51.1	42.85	45.2	37.95	35.4	37.15
Zirconium Carbonate	9.22	8.94	8.15	7.93	---	---
Titania(Not Rutile)	26.3	25.75	23.6	22.8	23.0	22.35
Lithium Carbonate	24.7	21.2	21.8	21.04	21.2	20.62
Alumina	---	32.9	---	24.1	---	23.45

TABLE II

Experimental Values for Viscosities of Individual Glasses

Glass Batch No. 47B

Temp. (°C)	Viscosity (poises)
1015	2060
1043	1390
1048	1100
1067	855
1086	397
1091	360
1115	230
1132	170

Glass Batch No. 49B

Temp. (°C)	Viscosity (poises)
967	5000
988	2600
1000	1755
1025	1192
1056	555
1090	278
1110	180

Glass Batch No. 50B

Temp. (°C)	Viscosity (poises)
924	4600
947	2000
968	1150
980	970
1004	273
1025	210
1030	177

Glass Batch No. 56

Temp. (°C)	Viscosity (poises)
928	1265
948	1007
963	780
979	600
1000	402
1029	263
1012	385
1050	230
1068	175

Glass Batch No. 66

Temp. (°C)	Viscosity (poises)
1304	510
1324	215
1326	205

Glass Batch No. 68

Temp. (°C)	Viscosity (poises)
1255	2090
1272	940
1300	475
1312	292
1320	205
1330	207
1335	180
1352	165
1310	315

TABLE 11 (Cont'd)

Glass Batch No. 72

Temp. (°C)	Viscosity (poises)
1142	2500
1160	1727
1184	1055
1200	860
1218	583
1228	325
1260	200

Glass Batch No. 74

Temp. (°C)	Viscosity (poises)
1240	5300
1246	1695
1259	1053
1262	594
1275	279
1300	207

Glass Batch No. 75

Temp. (°C)	Viscosity (poises)
1078	577
1088	433
1100	327
1105	275
1133	193

Glass Batch No. 76

Temp. (°C)	Viscosity (poises)
1182	5300
1192	1400
1201	972
1206	757
1210	300
1221	210
1230	155
1231	150

Glass Batch No. 77

Temp. (°C)	Viscosity (poises)
1302	1805
1310	1018
1315	683
1320	650
1322	396
1329	229

Glass Batch No. 97

Temp. (°C)	Viscosity (poises)
1118	1850
1145	860
1153	697
1173	540
1185	225
1195	197

Glass Batch No. 98

Temp. (°C)	Viscosity (poises)
1111	2500
1132	1135
1145	833
1160	487
1176	272
1200	177

TABLE III

Summary of Experimental Viscosity Determinations

Batch	Temperature at Which Viscosity is Approximately 300 Poises (°C)	Batch	Temperature at Which Viscosity is Approximately 300 Poises (°C)
1	1305	52	1088
24	1450	56	1026
25	1470	63-2	1269
31	1342	64	1326
32	1455	65	1267
41	925	66	1317
43	1060	68	1312
45	1170	72	1230
46	1254	74	1275
47B	1103	75	1102
48	1110	76	1210
49	1087	77	1327
49B	1087	97	1182
50	1067	98	1174
50B	1003		

TABLE IV

Rate of Growth of Cordierite in Batch 1

Observation No.	Temperature	Rate of Growth microns/min.
1	1339 ± 7	29
2	1189 ± 4	480
3	1415 ± 3	-20
4	1343 ± 4	11
5	1278 ± 4	210
6	1139 ± 4	360
7	1154 ± 6	315
8	1025 ± 5	33
9	962 ± 5	5
10	1278 ± 6	285
11	1407 ± 7	12
12	1411 ± 5	no growth in 5 min.
13	1395 ± 6	no growth in 9 min.
14	1355 ± 5	5
15	1220 ± 2	485

TABLE V

Experimental Values of Young's Modulus for Bulk Glass Samples Determined by Sonic Methods

Batch	Average Modulus ($x10^5$ kg/cm^2)	Average Modulus ($x10^6$ psi)	Batch	Average Modulus ($x10^5$ kg/cm^2)	Average Modulus ($x10^6$ psi)
1	10.46	14.86	52	7.64	10.87
4	10.50	14.94	63	10.34	14.71
14	10.60	15.07	64	10.96	15.57
24	7.51	10.67	64(repeat)	10.39	14.78
26	7.17	10.18	65	10.69	15.20
27	8.11	11.53	66	10.65	15.14
29	9.86	14.02	68	10.79	15.36
41	7.62	10.83	70	10.72	15.23
42	7.61	10.82	72-2	10.64	15.15
43	7.23	10.27	72-3	10.62	15.14
45	7.79	11.08	73-2	10.63	15.14
46B	7.31	10.40	76	8.11	11.51
47	7.78	11.07	77	8.55	12.16
47B	8.18	11.62	97	7.63	10.86
48B	7.94	11.28	98	7.47	10.62
49B	7.57	10.77	99	7.98	11.37
50	7.81	11.10	114	11.6	16.5
50B	7.64	10.83	117	11.62	16.54
51	8.26	11.75	138	11.62	16.53

TABLE VI

Circularity Checks on Mechanically Drawn Glass Fibers

Specimens were checked for roundness by rotating under a microscope, readings were made approximately 45° apart. All measurements are in mils.

Glass Fiber 70-3		Glass Fiber 72-3		
Specimen A	Specimen B	Specimen A	Specimen B	Specimen C
1.98	1.94	1.36	2.15	4.87
1.93	1.93	1.34	2.13	4.87
1.96	1.96	1.34	2.12	4.87
1.98	1.94	1.34	2.13	4.86
1.95	1.95	1.39	2.12	4.89
1.94	1.98	1.36	2.15	4.87
1.93	1.98	1.30	2.13	4.83
1.98	1.99	1.34	2.13	4.84

TABLE VII

Experimental Values for Young's Modulus for Mechanically Drawn Glass Fiber Samples Determined by Sonic Methods

Batch	Density ρ gms/cm^3	Velocity(c) cm/secx10^5	c^2 cm^2/sec^{2}x10^{10}	Young's Modulus (E) ρc^2 kg/cm^{2}x10^5	psix10^6	E/ρ psix10^6 gm/cm^3	Tested At
40-3		5.74	32.9				FAB
56-1	2.4368	5.79	33.5	8.18	11.63		FAB
62-3	2.7036	6.51	42.3	11.43	16.25	6.02	FAB
63-2	2.67	6.37	40.5	10.82	15.4	5.77	FAB
64	2.69	6.26	39.2	10.56	15.02	5.58	FAB
65	2.72	6.24	39.0	10.62	15.10	5.56	FAB
66	2.66	7.268					UARL
67-3	2.6535	6.58	43.25	11.48	16.33	6.17	FAB
68-2	2.6295	6.58	43.4	11.57	16.35	6.22	FAB
69	2.5910	6.39	40.9	10.58	15.05	5.81	FAB
70	2.73	6.58	43.2	11.78	16.77	6.14	FAB
71		7.311					UARL
72-4	2.85	6.06	36.75	10.47	14.87	5.21	FAB
73	2.97	6.125	37.5	11.14	15.85	5.33	FAB
82-2*	2.5875	6.49	42.1	10.89	15.47	5.98	FAB
83-1**	2.8376	6.53	42.6	12.08	17.18	6.07	FAB
102		5.45					UARL
114	3.18	6.12	37.5	11.93	17.0	5.38	FAB
126	3.4634	6.00	36.0	12.45	17.75	5.13	FAB
127	3.2553	6.06	36.75	11.92	16.98	5.22	FAB
129	3.3105	6.03	36.4	12.03	17.12	5.17	FAB
131		5.89	34.7				FAB
135	2.6303	6.16	37.9	9.98	14.19	5.38	FAB
136	2.8035	6.08	36.9	10.35	14.72	5.26	FAB
137	3.0834	6.08	37.0	11.4	16.23	5.27	FAB
138	3.51	5.66	30.9	10.83	15.42	4.38	FAB
140		6.208					UARL

* Prepared from the prescription and teachings contained in Jason D. Provance, U.S. 3,044,888

** Prepared from the prescription and teachings contained in Ralph L. Tiede, U.S. 3,127,277, Example 4 by UARL for direct comparative testing.

TABLE VIII

Experimental Value for Young's Modulus for Mechanically Drawn Glass Fibers Determined by Mechanical Testing

Glass Batch 114 (File F-122-67)

Five specimens were tested. Twelve measurements of diameter were made along the length for each specimen.

Average Diameter (mils)	Diameter Ranae (mils)	Young's Modulus (10^6 psi)
1.25	1.20 - 1.30	16.5
1.09	1.05 - 1.15	17.2
1.07	1.05 - 1.10	16.7
1.05	1.00 - 1.10	18.2
1.01	0.95 - 1.10	18.6
	Average	17.4
	Comparative Sonic Value - Table VI	17.0

FIG, 1

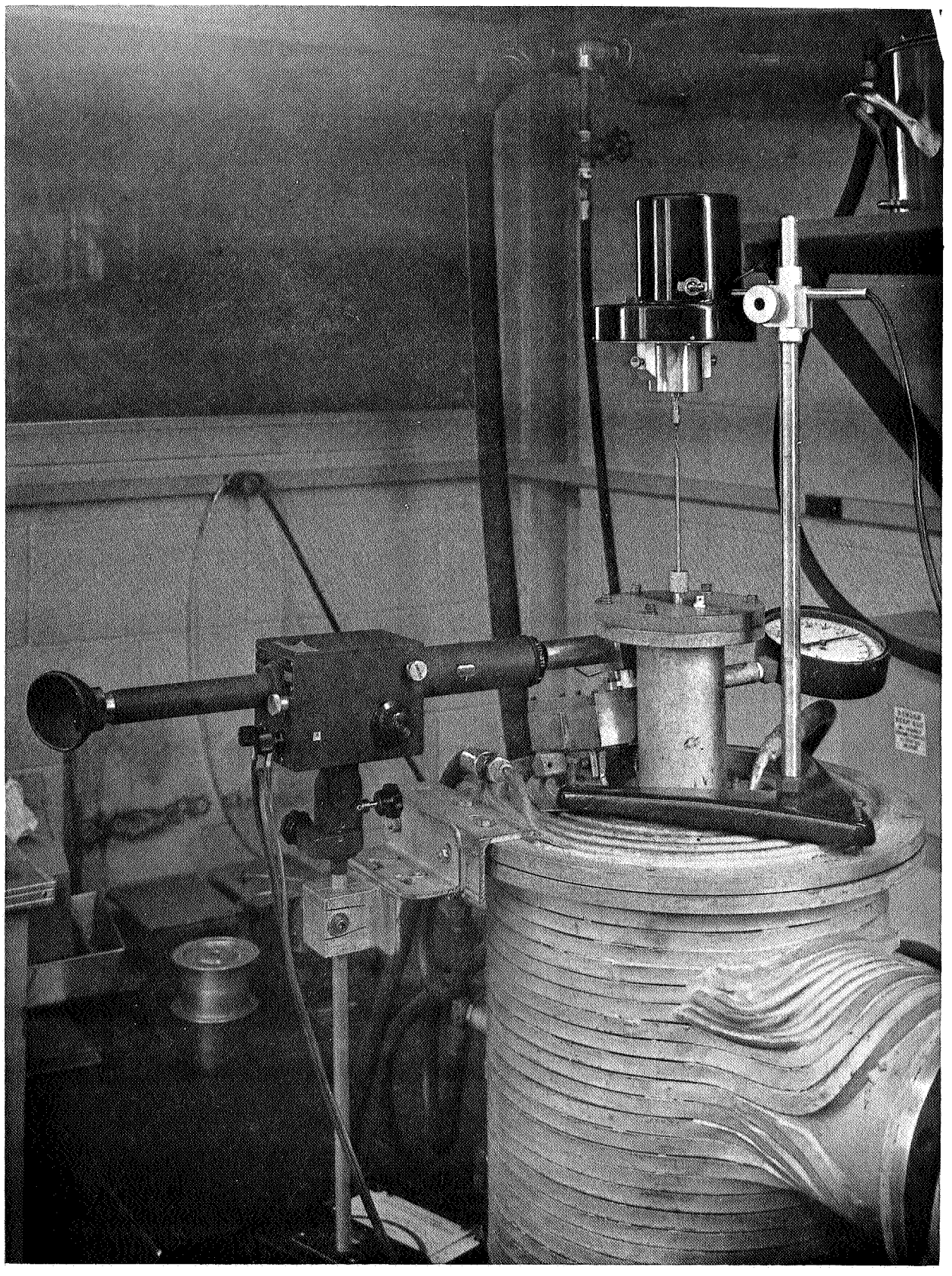
PREPARATION OF EXPERIMENTAL GLASSES

67-186C

F910373-7

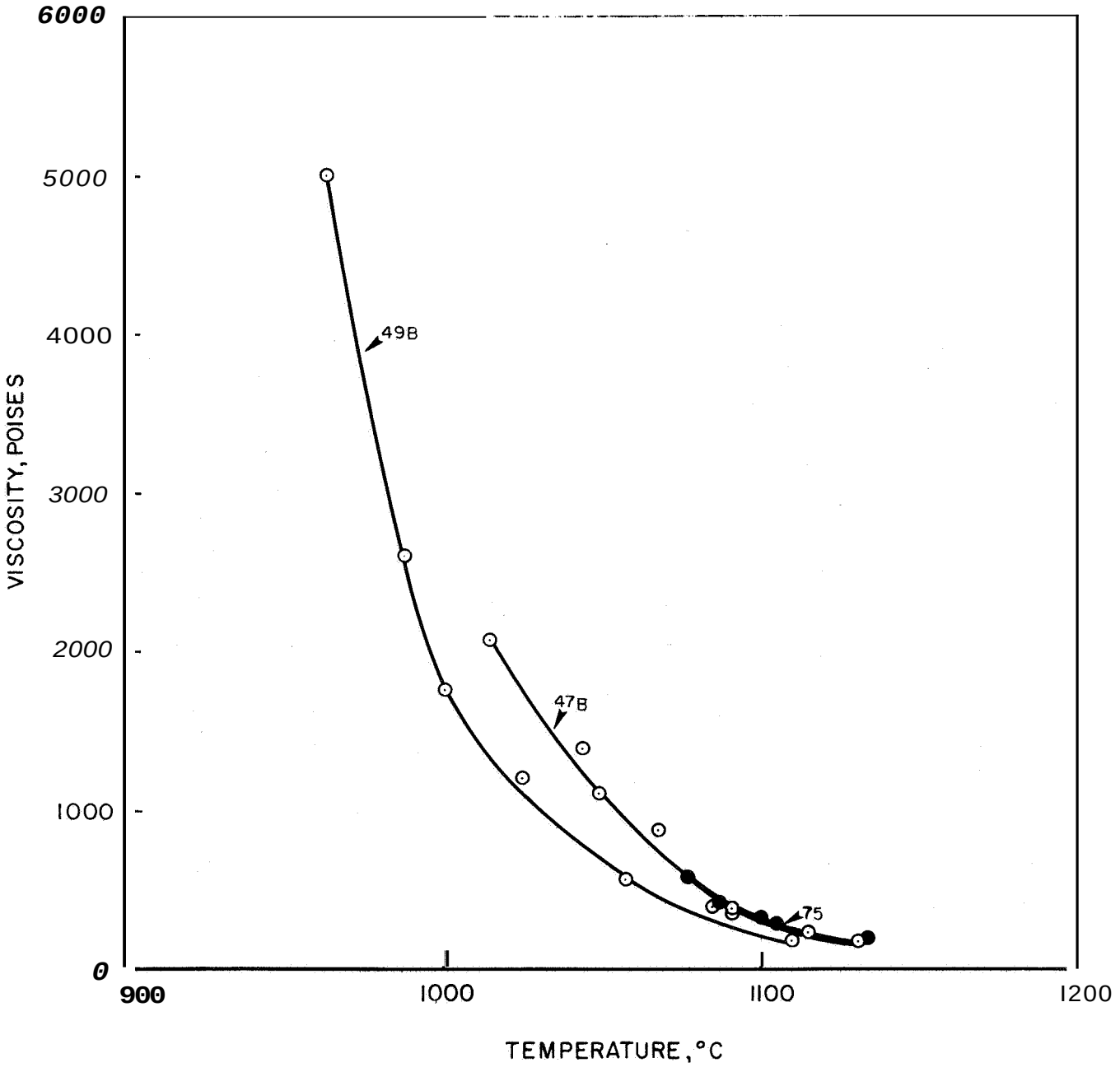
FIG. 2

BROOKFIELD VISCOMETER INSTALLED ON TUNGSTEN FURNACE FOR HIGH TEMPERATURE VISCOSITY MEASUREMENTS



FIG, 3

EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



FIG, 4

EXPERIMENTALLY DETERMINED VISCOSITY – TEMPERATURE RELATIONS

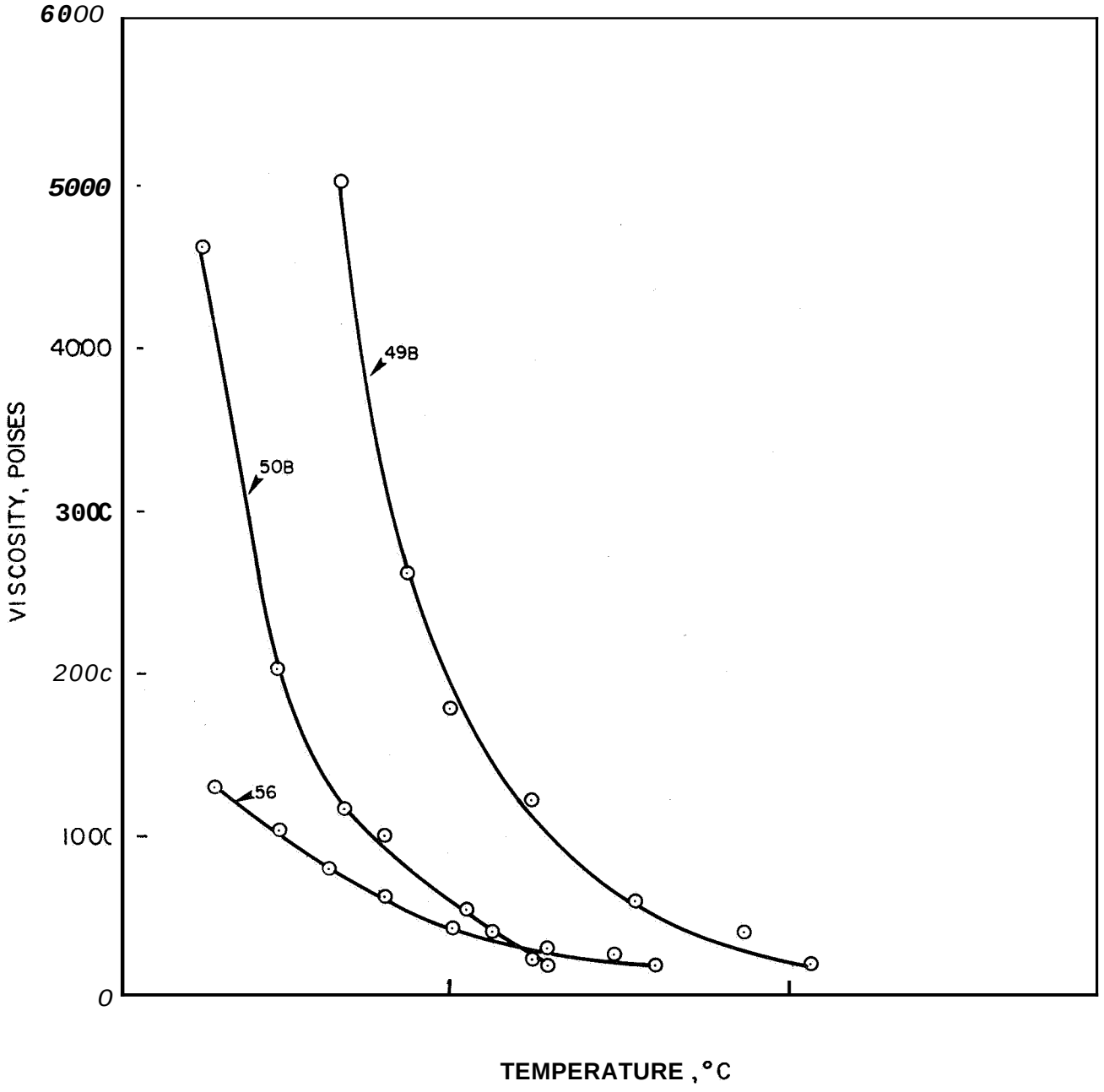


FIG. 5

EXPERIMENTALLY DETERMINED VISCOSITY - TEMPERATURE RELATIONS

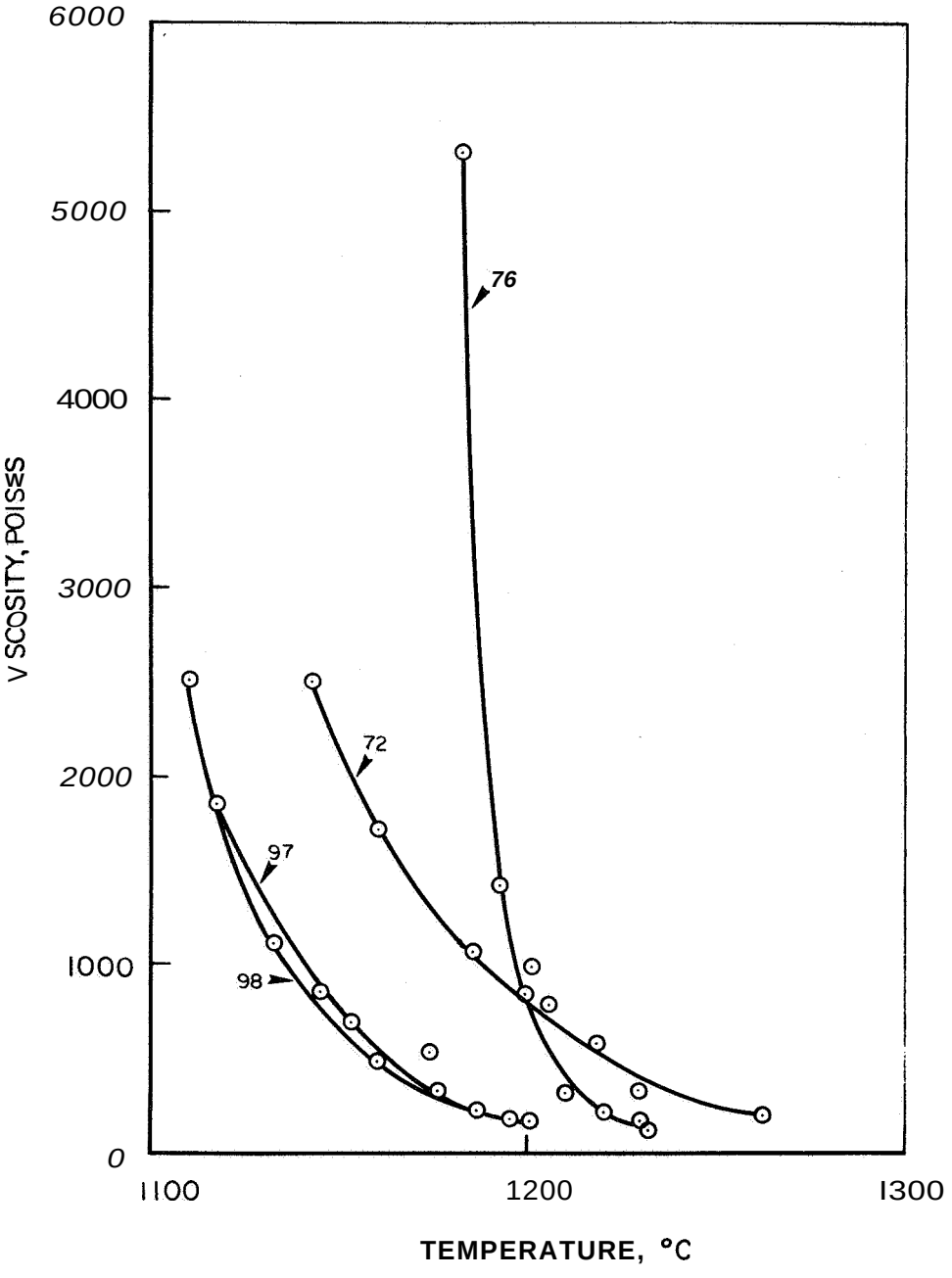


FIG. 6

EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS

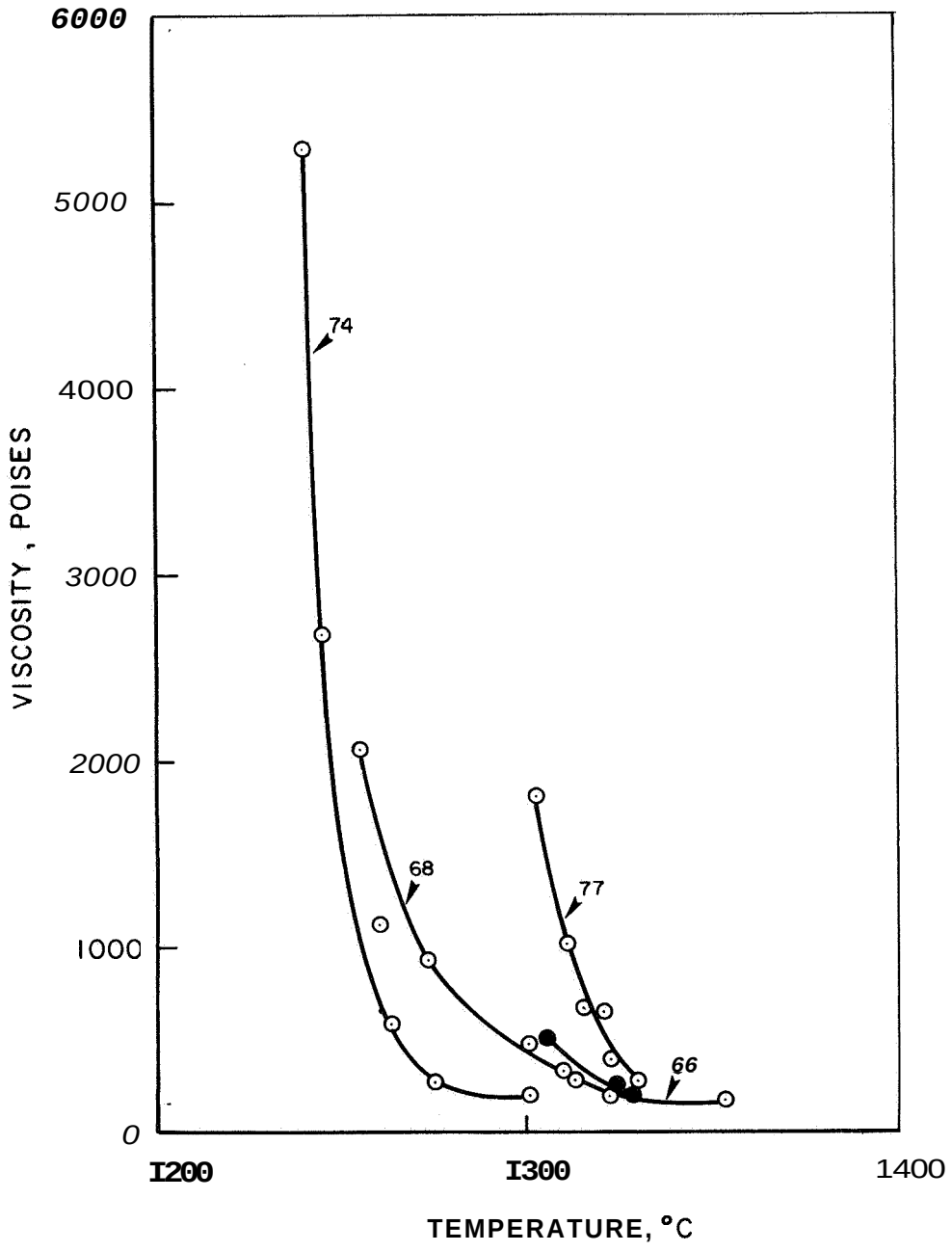
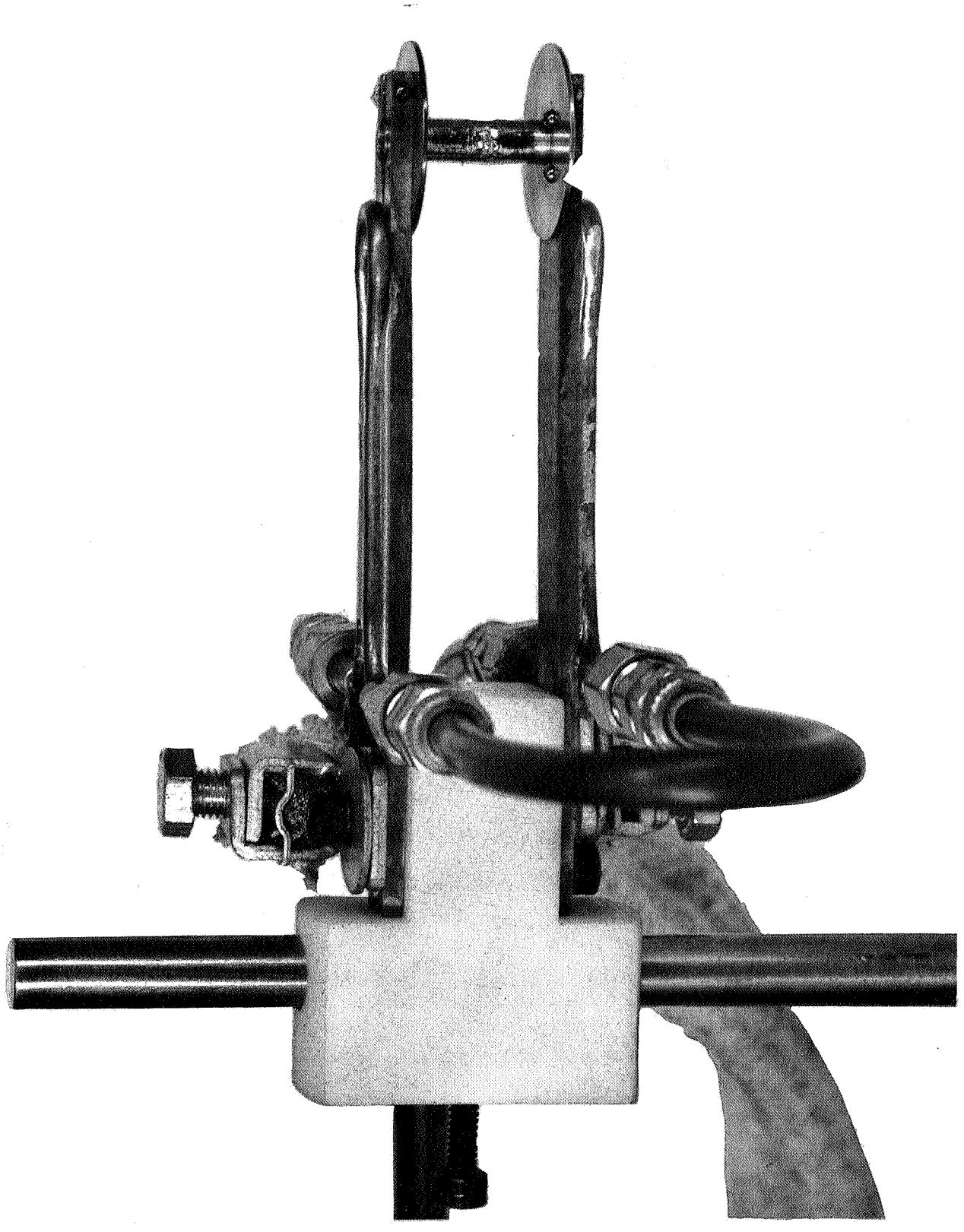


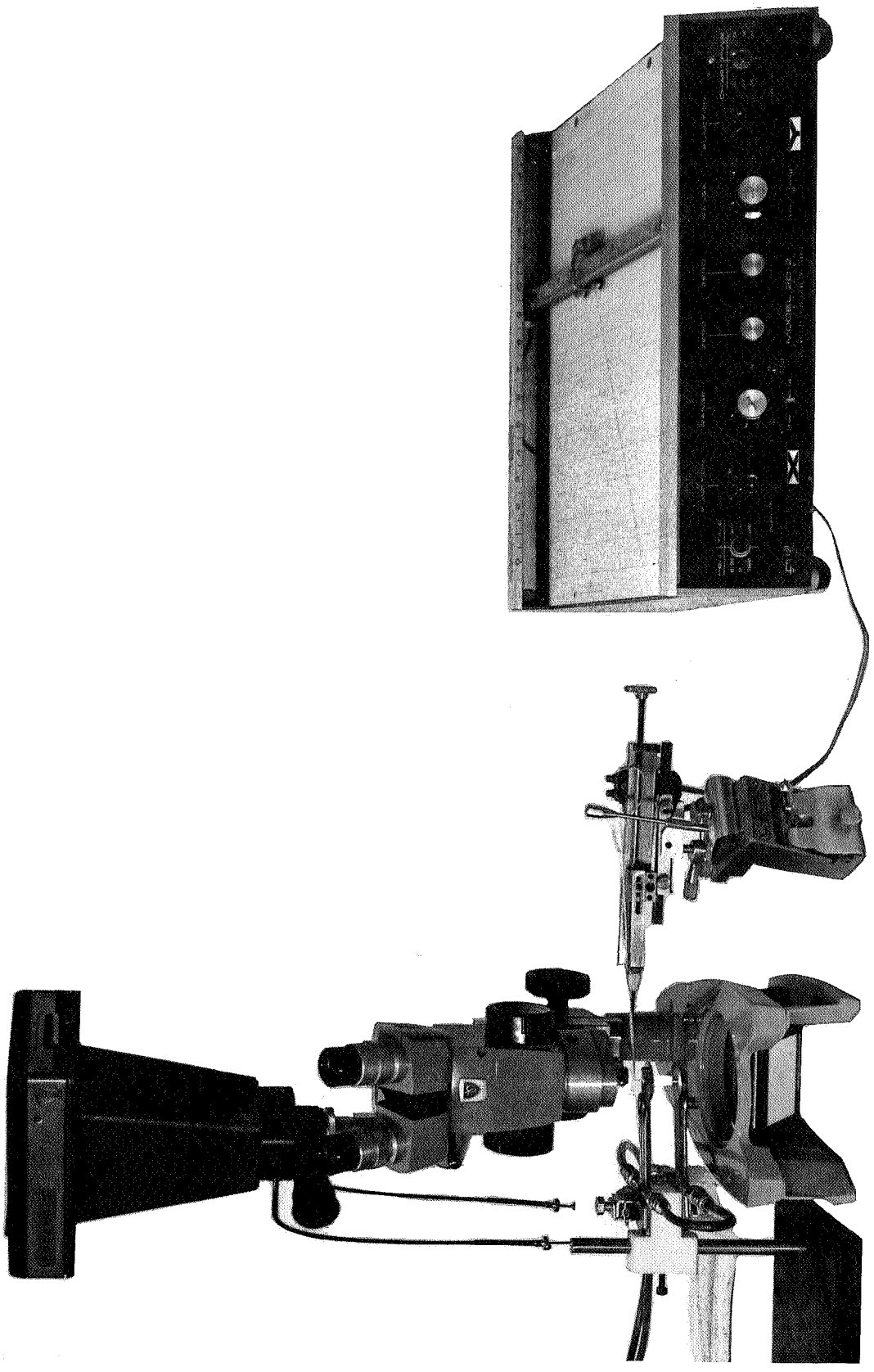
FIG. 7

CLOSE-UP OF MICRO-FURNACE HEAT SHIELDS REMOVED



66-373-B

FIG. 8



MICRO-FURNACE IN POSITION FOR USE

66-373- A

F910373-7

FIG.9

EFFECT OF TEMPERATURE UPON THE RATE OF GROWTH OF CORDIERITE

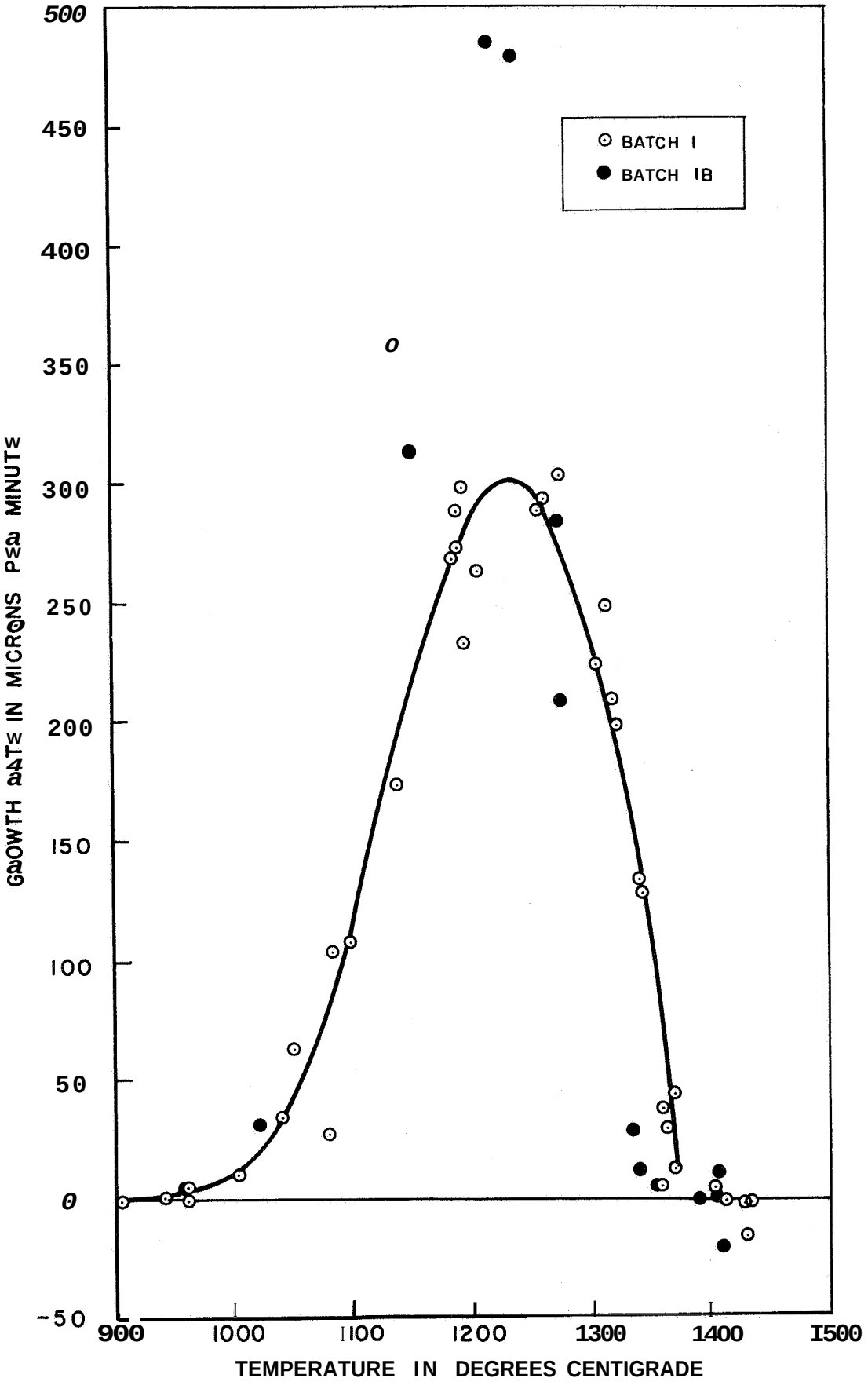
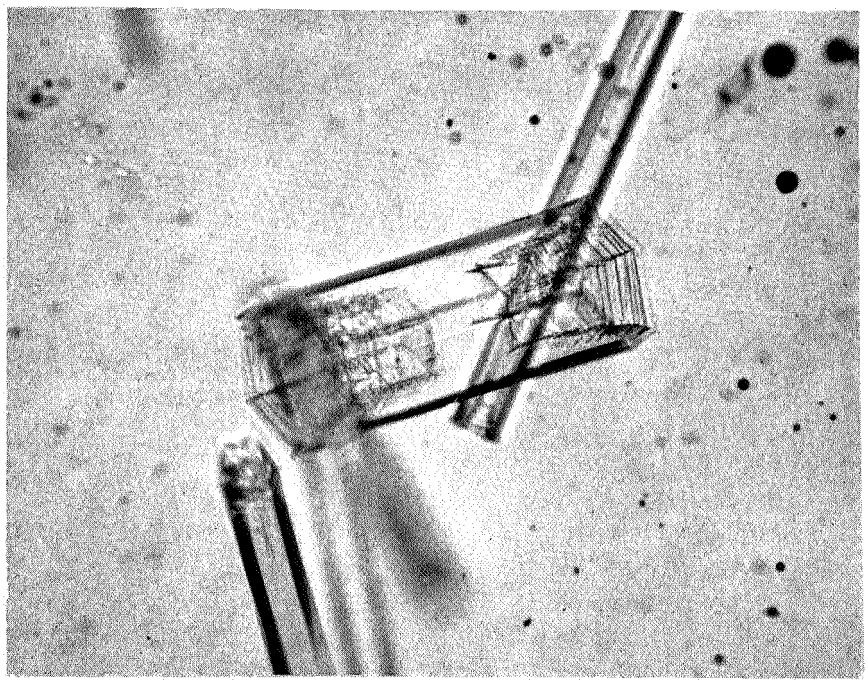


FIG. 10

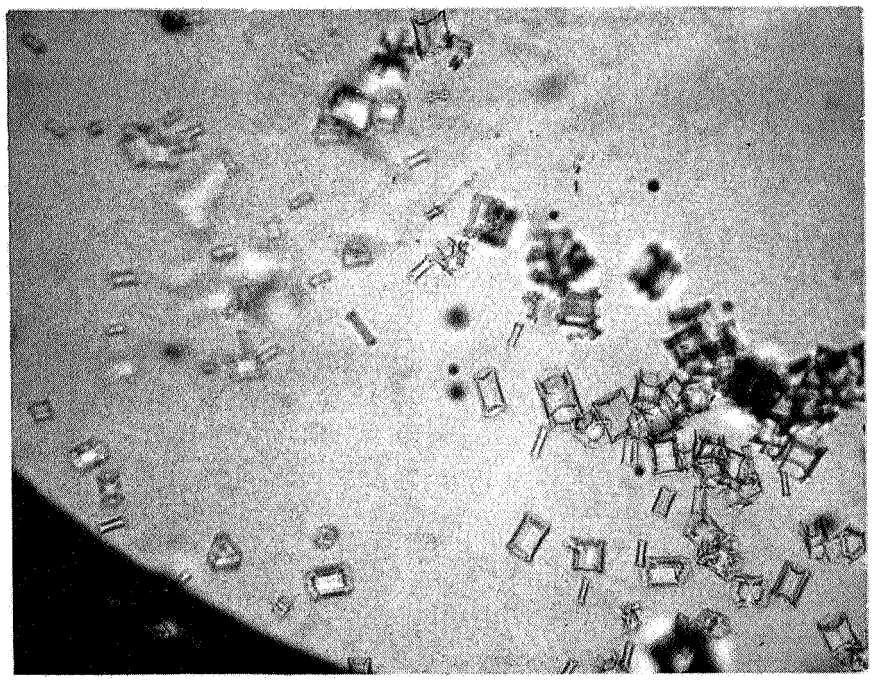
CORDIERITE CRYSTALS IN GLASS



MAGNIFICATION: 100X

FIG. 11

CORDIERITE CRYSTALS IN GLASS



MAGNIFICATION: 100X

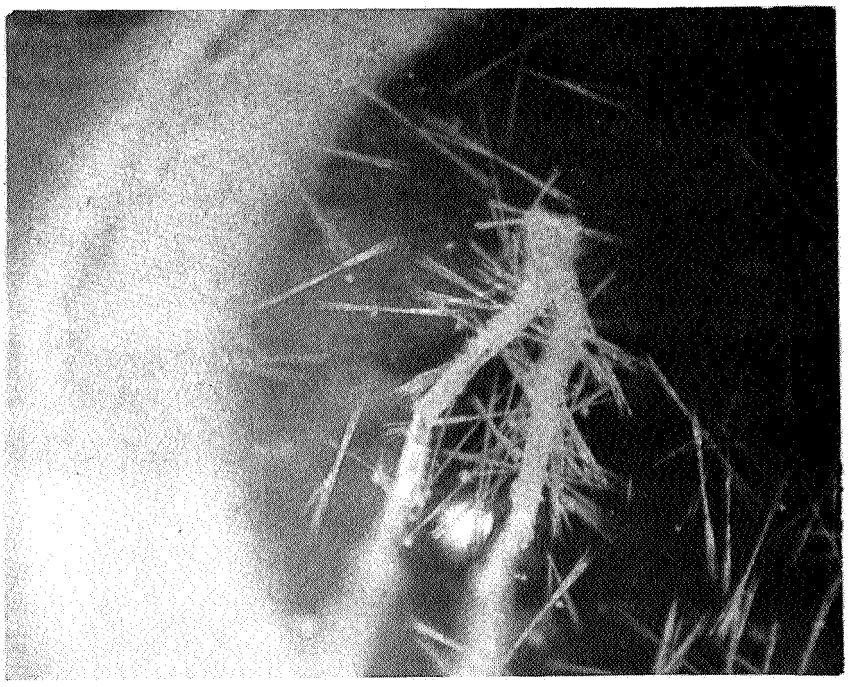
FIG. 12

SAPPHIRINE CRYSTALS IN GLASS

MAGNIFICATION: 200X

FIG. 13

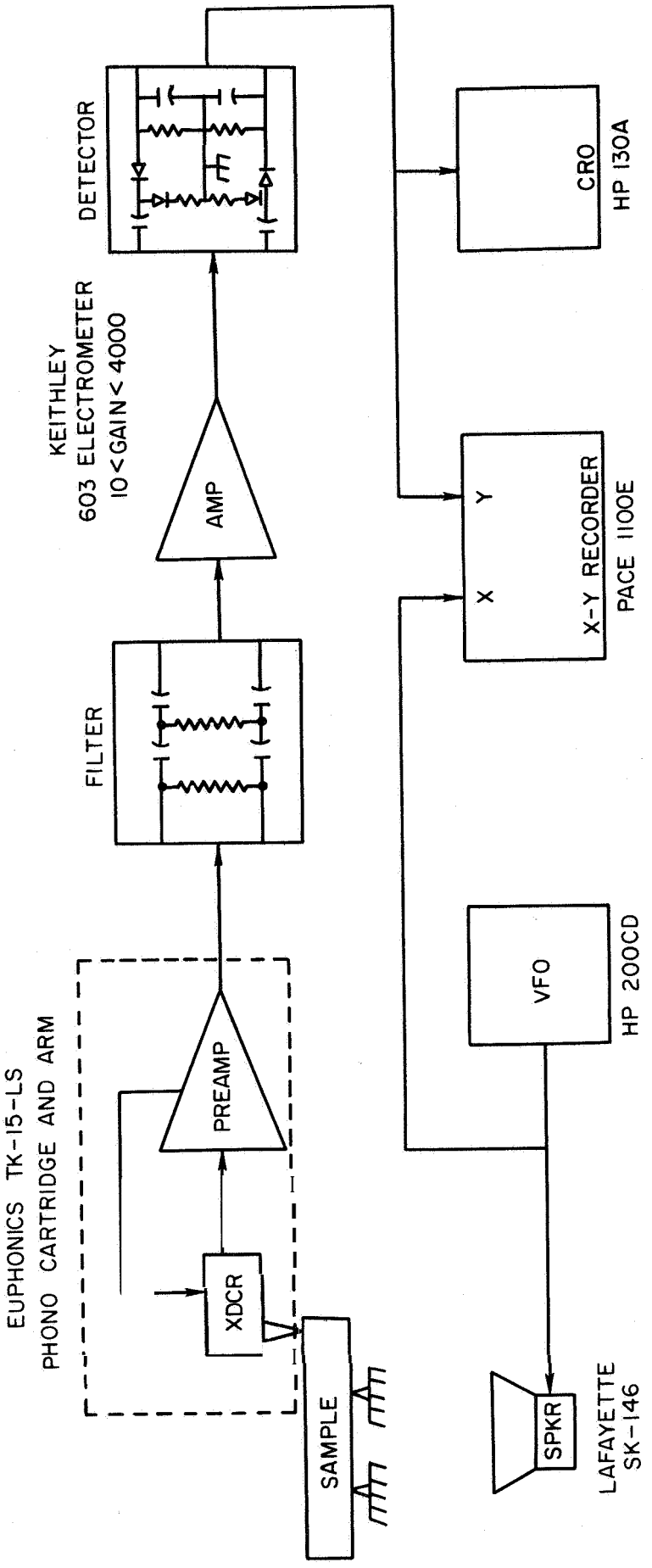
SAPPHIRINE CRYSTALS IN MOLTEN GLASS AT 1222°C



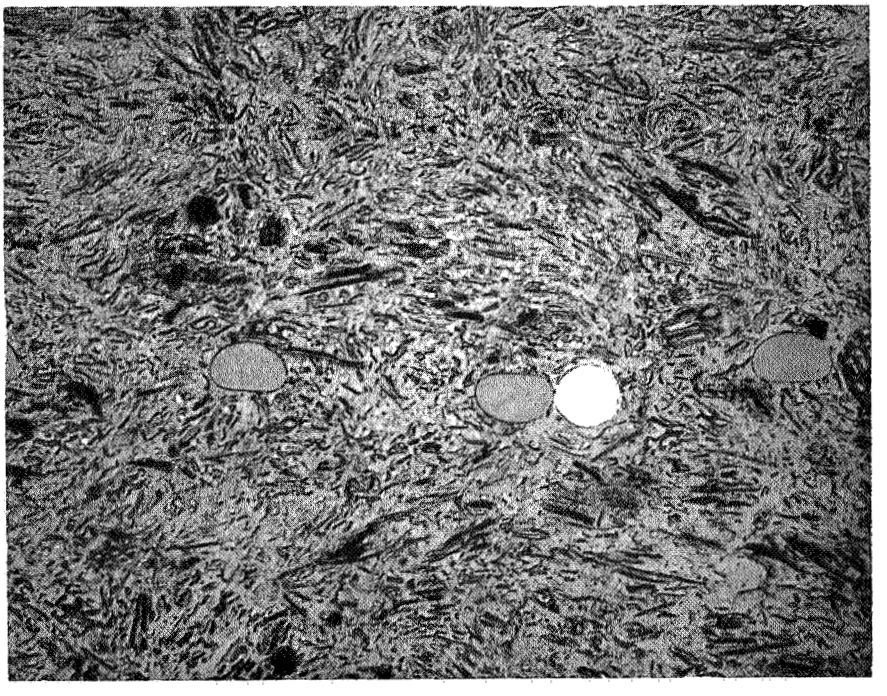
MAGNIFICATION: 40 X

FIG. 14

IMPROVED APPARATUS USED FOR THE MEASUREMENT OF YOUNG'S MODULUS



CROSS-SECTION OF HAND-DRAW GLASS FIBERS SHOWING THE LEAST DEPARTURE FROM CIRCULAR CROSS-SECTION COMPARED TO A PLATINUM WIRE (WHITE DOT).
100X IN ORIGINAL PHOTOGRAPH



CROSS-SECTION OF HAND-DRAWN GLASS FIBERS SHOWING THE MOST DEPARTURE FROM CIRCULAR CROSS-SECTION COMPARED TO A PLATINUM WIRE (WHITE DOT).
100X IN ORIGINAL PHOTOGRAPH

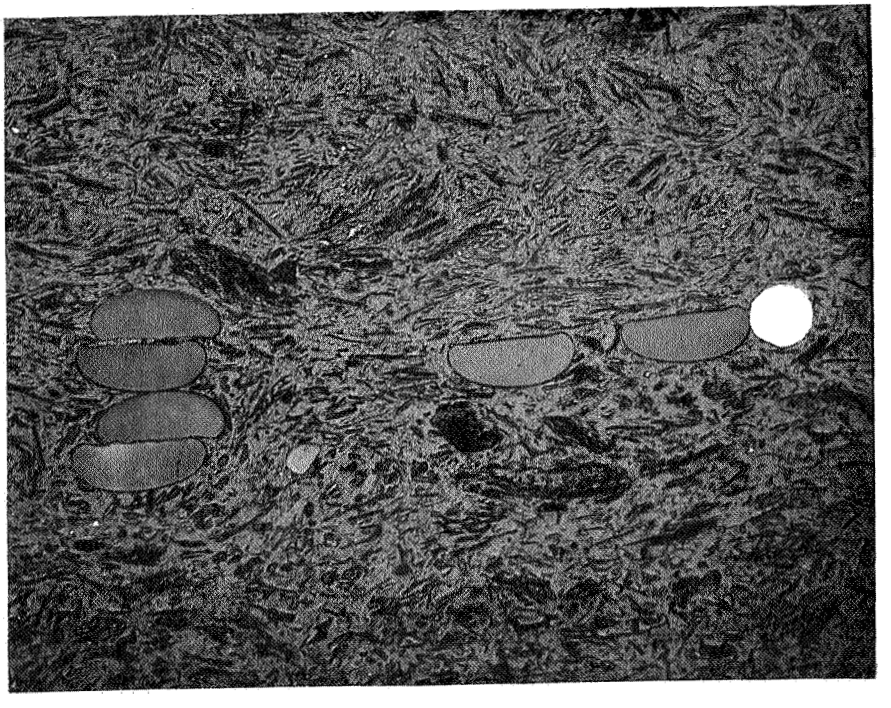
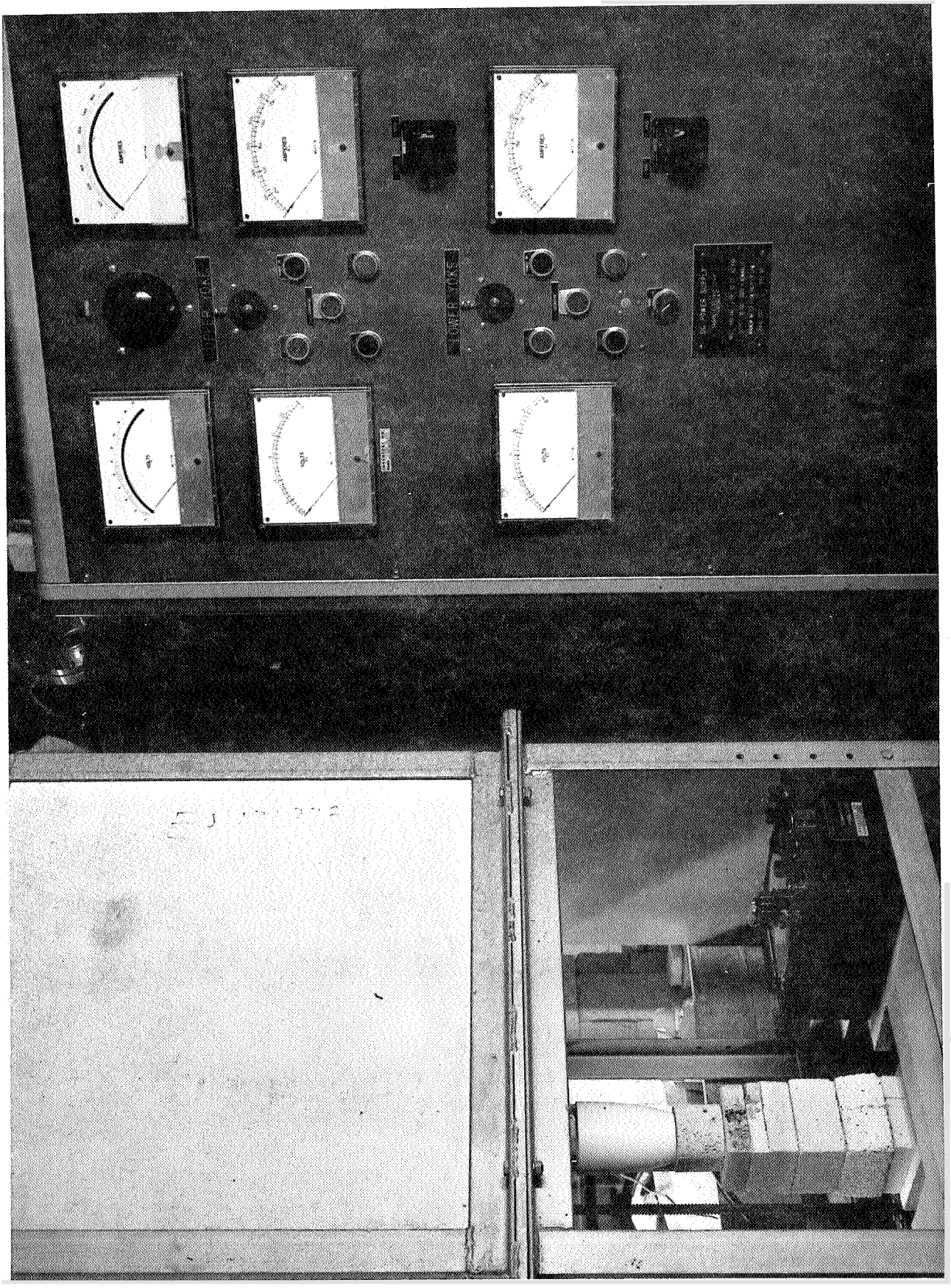
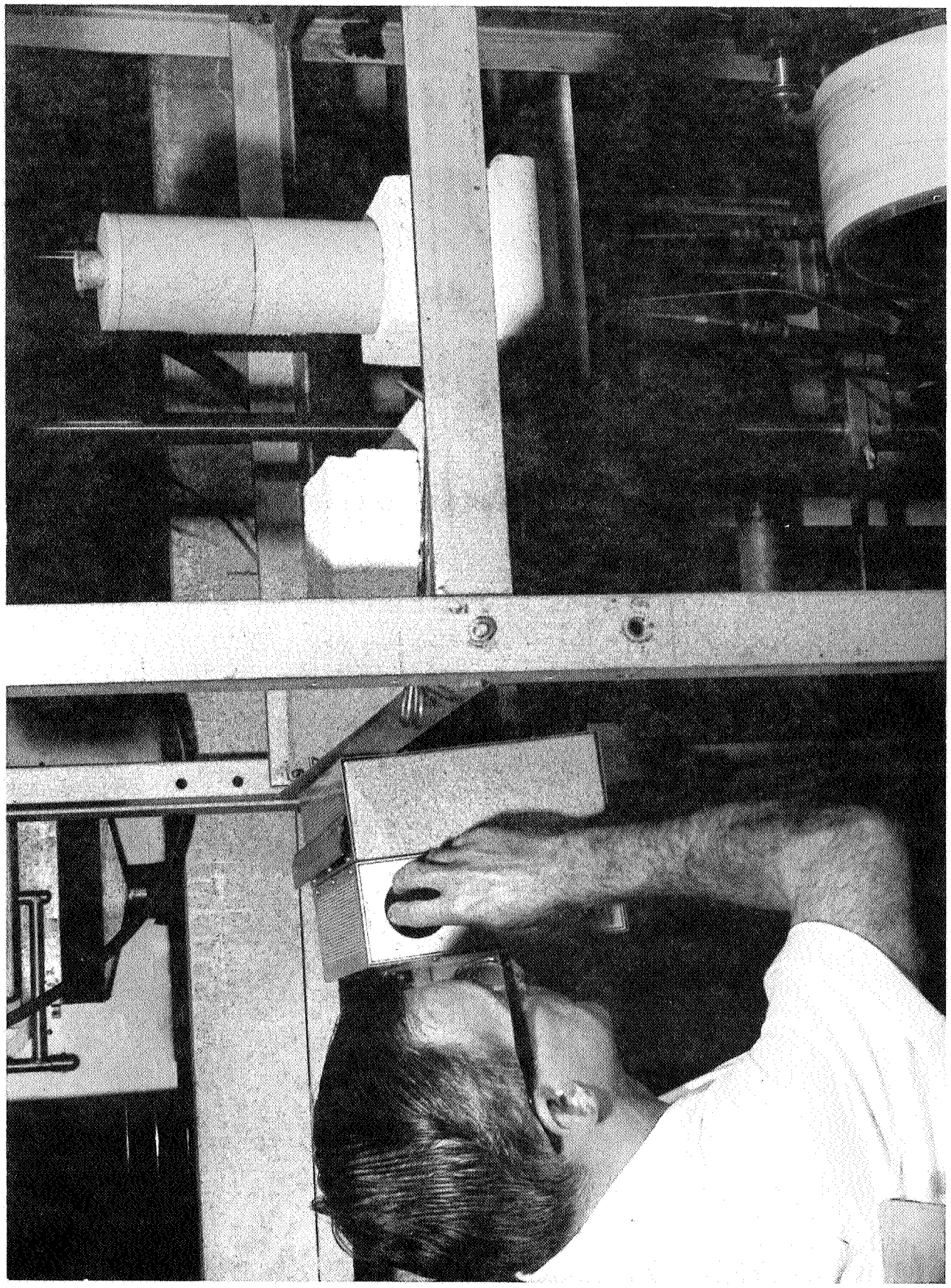


FIG. 17

IMPROVED PLATFORM KILN

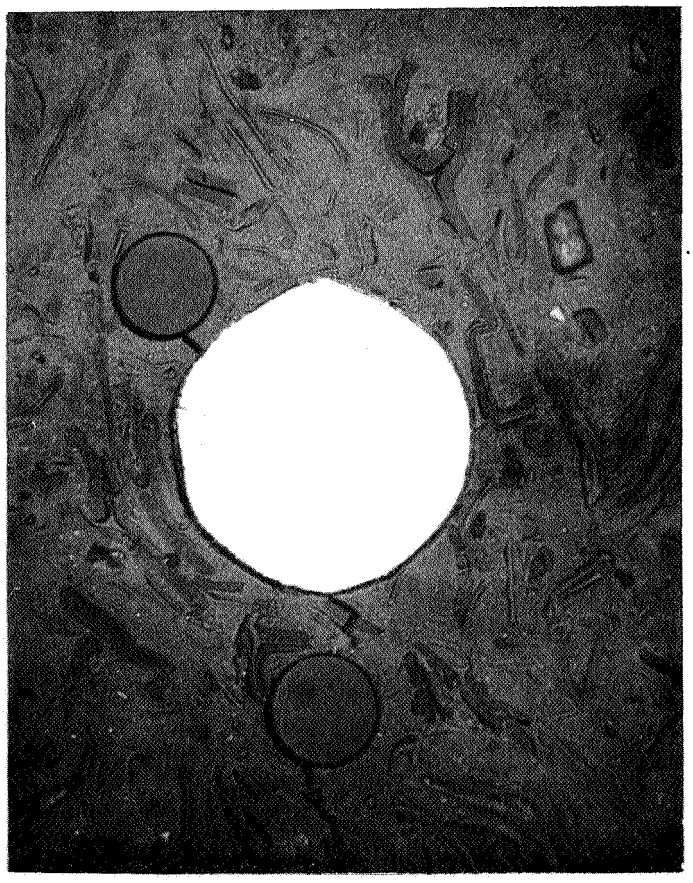


PLATFORM KILN IN USE FOR MECHANICALLY DRAWING GLASS FIBERS



67-186 A

PRONOUNCED DECREASE IN SIZE AND IMPROVEMENT IN CIRCULARITY OF MACHINE DRAWN FIBERS



MAGNIFICATION: 500X

FIG. 20

PRONOUNCED DECREASE IN SIZE AND IMPROVEMENT IN CIRCULARITY OF MACHINE DRAWN FIBERS

MAGNIFICATION: 500X

SONIC VELOCITY MEASUREMENT EQUIPMENT RENTED FROM H.M. MORGAN CO., INC.

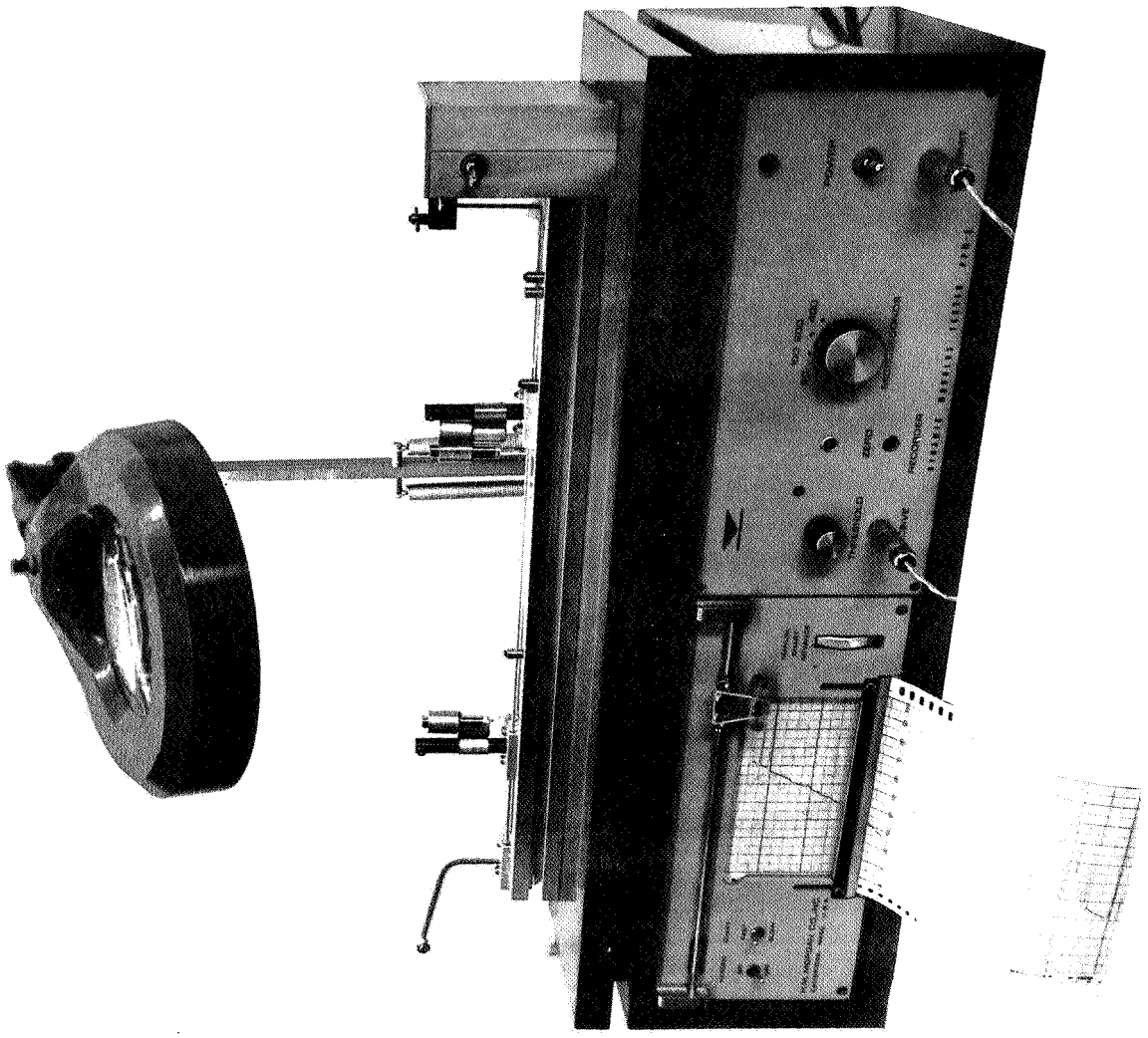


FIG.22

NEW VACUUM AND/OR INERT ATMOSPHERE FURNACE FOR CASTING GLASS SAMPLES